

# PATENT SPECIFICATION

(11) 1 517 910

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1517910

(21) Application No. 52807/74 (22) Filed 6 Dec. 1974  
 (23) Complete Specification filed 21 Nov. 1975  
 (44) Complete Specification published 19 July 1978  
 (51) INT CL<sup>2</sup> C08K 7/18  
 (52) Index at acceptance C3K 111 230 400 MA  
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## (54) VINYL HALIDE POLYMER COMPOSITION

(71) We, BP CHEMICALS INTERNATIONAL LIMITED., of Britannic House, Moor Lane, London, EC2Y 9BU, a British company, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

10 The present invention relates to a polymer composition and particularly to a vinyl halide paste forming polymer composition.

15 Paste forming vinyl halide polymers are well known. They are derived from vinyl halide polymer latices. The polymers are normally recovered from such latices by spray-drying. They are then generally ground and mixed with plasticisers to form pastes which can be spread or moulded and finally formed into fabricated solid products by heating. A very important property of the pastes is the paste viscosity, which for example in a high speed coating process 20 largely controls the speed at which the paste can be spread. This is known to be controlled to a large extent by the particle size distribution of the paste forming polymer particles and British Patent 680,226 shows that paste viscosity may be reduced by 25 adding a vinyl chloride — vinylidene chloride copolymer powder of particle size in the range 300—500 B.S. mesh. The letters B.S. referred to in connection with mesh size signify throughout this specification British Standard. The relevant British Standard is B.S. 410.

30 Accordingly the present invention provides a polymer composition comprising a paste forming vinyl halide polymer in admixture with an inert solid material as defined herein in the form of substantially spherical particles having an average particle size greater than that of the paste forming vinyl halide polymer but not greater than 250  $\mu\text{m}$ .

35 Any vinyl halide polymer capable of forming a free flowing paste when admixed with a plasticiser may be used. Such

polymers generally have a particle size in the range 0.5 to 5  $\mu\text{m}$  and are usually prepared by spray-drying a vinyl halide latex prepared by emulsion or microsuspension polymerisation.

40 The preferred vinyl halide is vinyl chloride or a copolymer of vinyl chloride with not more than 20% of a copolymerisable monomer. Examples of such monomers are ethylene, propylene, vinyl acetate, vinyl laurate, vinyl stearate and vinylidene chloride.

45 By an inert solid material is meant a substance other than a vinyl halide polymer or copolymer that is insoluble in plasticiser and which does not absorb more than 20% wt. and preferably less than 10% wt. of plasticiser at room temperature and which does not react chemically with vinyl halide polymer in the paste. Suitable materials are glasses. Other suitable materials are described as synthetic silicates, (which may or may not be glasses).

50 By average particle size is meant in this specification the weight mean particle diameter. This is the particle diameter below and above which 50% by weight of the polymer occurs. It may be determined by a Coulter Counter or disk centrifuge.

55 It is preferred to use inert solid materials having an average particle size not less than 10  $\mu\text{m}$ , more preferably not less than 20  $\mu\text{m}$ . A particularly preferred material is glass spheres sold under the trade name Ballotini. It is preferred to use glass spheres having a particle size distribution of 80% by weight between 4 and 44 microns and having an average particle size between 30 and 40  $\mu\text{m}$  e.g. about 34.5  $\mu\text{m}$ . When glass spheres are employed it may be desirable to coat them with a coupling agent to render them more compatible with vinyl halide polymer. Suitable coupling agents include silanes and surfaces by the polymer. Such agents are well-known in connection with the glass fibre reinforcement of thermoplastic polymers. Such coatings are not used to affect the viscosity of the paste but to facilitate the incorporation of the glass

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5	spheres into the polymer plasticiser mixture when the paste is heated to gel it. For the purposes of viscosity reduction in the paste before heating the glass spheres should be inert in the paste.	meter model RVF was used for the measurements and the results shown in Table 2 were calculated in terms of thixotropic Breakdown Co-efficient (B), apparent viscosity at 4 r.p.m. (approximating to 1 sec. <sup>-1</sup> ) and non-Newtonian index (n) assuming the pastes to be power law fluids following the procedure of Johnston & Brower (SPE Journal, November 1966 p.45) but modifying the calculation constants to enable the results to be expressed in SI units.	50
10	Preferably the amount of inert solid is not more than 30% by weight of the total weight of inert solid and vinyl halide polymer. Most preferably the amount of inert solid lies in the range 10—20% wt. of the total weight.	Breon P130/1 (Registered Trade Mark) is a conventional paste forming vinyl chloride homopolymer. It has an average particle size (weight mean particle diameter) of about 2 $\mu$ m.	55
15	The solid may be simply mixed with the vinyl halide polymer. The composition of the present invention may be formed into pastes by admixture with plasticisers in known fashion. Conventional ingredients of vinyl halide paste polymer systems may also be incorporated.	Breon CS100/30 (Registered Trade Mark) is well-known viscosity reducing additive polymer of the type described in Brit. Pat. 680,226, i.e. it is a powdery vinyl chloride-vinylidene chloride copolymer of large particle size.	60
20	Examples of plasticisers and other ingredients are di-n-butyl phthalate, di-isobutyl phthalate, di-2-ethyl hexyl phthalate, phthalates of mixed C <sub>10</sub> to C <sub>18</sub> alkyl alcohols, adipate of C <sub>10</sub> —C <sub>18</sub> alkyl alcohols, di-2-ethyl hexyl sebacate, tri-tolyl phosphate, tri-xylyl phosphate, epoxidised soya bean oil, as plasticisers; chlorinated paraffins and aromatic petroleum residues as secondary plasticiser; calcium stearate, basic lead carbonate, dibutyl tin dilaurate, and complex mixtures of alkyl or aryl carboxylic acid salts of barium, cadmium, calcium and zinc as stabilisers. White spirit or other mineral spirits can be used as diluents and the composition can be coloured using titanium dioxide and other colour pigments such as phthalocyanines and some azoic types as typically used in PVC.	Omya BSH is a ground whiting filler with a particle size range of 80% within 1 $\mu$ m and 10 $\mu$ m.	65
25	The invention is illustrated by the following Comparative Tests A, B, C and by Examples 1 and 2.	Ballotini 2024 consists of spheres of soda glass with a particle size range 80% within 105 $\mu$ m and 210 $\mu$ m.	70
30	The ingredients for the recipes shown in Table 1 were blended together in a Hobart CE 100 (Registered Trade Mark) planetary mixer to from homogeneous pastes. These pastes were stored at 23°C in a constant temperature room and the viscosity characteristics were determined after storage periods of 1 hour, 48 hours and 168 hours. A Brookfield Synchroelectric Visco-	Ballotini 3000 is a similar product but with the glass spheres in the size range 80% within 4 $\mu$ m and 44 $\mu$ m.	75
35		The above values of particle size are those quoted by the manufacturer. A Coulter Counter test on Ballotini 3000 gave a weight mean particle diameter of 34.5 $\mu$ m.	80
40		Interstab M122 (Registered Trade Mark) is a proprietary liquid stabiliser based on a mixture of metal soaps.	85
45		Example 2 represents the use of the preferred additive.	90
		It will be seen that the preferred additive produces a greater viscosity reduction than the Breon CS100/30 whilst maintaining similar thixotropic and non-Newtonian characteristics in the paste. The conventional filler gave a paste with higher viscosity than the normal paste without additives.	95

TABLE 1  
Paste Compositions

Test	A	B	C	1	2
Breon P130/1	100	75	75	75	75
Breon CS100/30	—	25	—	—	—
Omya BSH	—	—	25	—	—
Ballotini 2024	—	—	—	25	—
Ballotini 3000	—	—	—	—	25
Di-2-ethyl hexyl phthalate	60	60	60	60	60
Interstab M122	2	2	2	2	2

TABLE 2  
Paste Rheology

Age of Paste	8 min Thixotropic Breakdown Coefficient		Non-Newtonian Index	Apparent Viscosity @ 4 r.p.m. (approx. 1 sec <sup>-1</sup> )
	days	B	n	Pa s
Test A (No additive)	0	0.0	0.8	16.3
	2	0.8	0.7	33.5
	7	0.6	0.7	38.0
Test B (Breon CS100/30)	0	0.1	0.8	9.0
	2	0.3	0.8	12.7
	7	0.4	0.8	13.8
Test C (Omya BSH)	0	0.3	0.6	23.9
	2	0.7	0.6	35.8
	7	0.6	0.6	42.7
Example 1 (Ballotini 2024)	0	0.1	0.7	9.4
	2	0.3	0.8	10.0
	7	0.4	0.8	10.9
Example 2 (Ballotini 3000)	0	0.1	0.8	7.9
	2	0.3	0.8	9.8
	7	0.3	0.8	10.8

WHAT WE CLAIM IS:—

5      1. A polymer composition which comprises a paste forming vinyl halide polymer in admixture with an inert solid material as hereinbefore defined in the form of substantially spherical particles having an average particle size greater than that of the paste forming vinyl halide polymer but not greater than 250  $\mu\text{m}$ .

10     2. A polymer composition according to Claim 1 wherein the vinyl halide polymer is a copolymer of vinyl chloride and not more than 20% of a copolymerisable monomer.

15     3. A polymer composition according to Claim 1 wherein the vinyl halide polymer is a vinyl chloride homopolymer.

4. A polymer composition according to any of the preceding claims wherein the inert solid material has an average particle size not less than 10  $\mu\text{m}$ .

5. A polymer composition according to Claim 4 wherein the inert solid material has an average particle size not less than 20  $\mu\text{m}$ .

6. A polymer composition according to any one of the preceding claims wherein the inert solid material is a glass.

7. A polymer composition according to any one of the preceding claims wherein the inert solid material is in the form of glass spheres.

8. A polymer composition according to Claim 7 wherein the glass spheres have an

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average particle size between 30 and 40  $\mu\text{m}$  and with 80% by weight of the particles between 4 and 44 microns.

9. A polymer composition according to 5 any one of the preceding claims wherein the amount of inert solid is not more than 30% by total weight of inert solid and vinyl halide polymer.

10. A polymer composition according to 10 Claim 9 wherein the quantity of inert solid is in the range 10 to 20% by weight of the total weight of inert solid and vinyl halide polymer.

11. A polymer composition according to 15 any one of the preceding claims, in the form of a plastisol.

12. A polymer composition substantially as hereinbefore described with reference to Examples 1 and 2.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.